PB86-212651

# Study of the Effects of Dry and Wet Deposition on Galvanized Steel and Weathering Steel: A Three Year Field Exposure

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

May 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-212651

EPA/600/D-86/115
May 1986

# A STUDY OF THE EFFECTS OF DRY AND WET DEPOSITION ON GALVANIZED STEEL AND WEATHERING STEEL: A THREE YEAR FIELD EXPOSURE

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**TECHNICAL REPORT DATA**
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| 1. REPORT NO. | 2. | 3. RECIPIENT'S ACCESSION NO. |
|---|---|---|
| EPA/600/D-86/115 | | |

| 4. TITLE AND SUBTITLE | 5. REPORT DATE |
|---|---|
| A STUDY OF THE EFFECTS OF DRY AND WET DEPOSITION ON GALVANIZED STEEL AND WEATHERING STEEL: A Three Year Field Exposure | May 1986 |
| | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) | 8. PERFORMING ORGANIZATION REPORT NO. |
| J.W. Spence, F.H. Haynie, D.C. Stiles and E.O. Edney | |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS | 10. PROGRAM ELEMENT NO. |
| (Same as Box 12) | CCVN1A/08/3002 (FY-86) |
| | 11. CONTRACT/GRANT NO. |
| 12. SPONSORING AGENCY NAME AND ADDRESS | 13. TYPE OF REPORT AND PERIOD COVERED |
| Atmospheric Sciences Research Laboratory - RTP, NC<br>Office of Research and Development<br>U.S. Environmental Protection Agency<br>Research Triangle Park, NC 27711 | 14. SPONSORING AGENCY CODE<br>EPA/600/09 |

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| | | |

| 18. DISTRIBUTION STATEMENT | 19. SECURITY CLASS *(This Report)* | 21. NO. OF PAGES |
|---|---|---|
| RELEASE TO PUBLIC | UNCLASSIFIED | 23 |
| | 20. SECURITY CLASS *(This page)* | 22. PRICE |
| | UNCLASSIFIED | |

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

## Abstract

At an exposure site located at the Research Triangle Park, NC, an automatic covering device was installed to partition the effects of dry and wet deposition on the corrosion of galvanized steel and weathering steel samples. Weight loss was used as the measure of corrosion of both metals. Meteorological parameters and air quality were recorded continuously during the 36-month exposure study and evaluated to eliminate errors and to estimate missing data. Models were derived to describe the corrosion of galvanized steel and weathering steel. Rainfall was found to be a significant factor for the corrosion of both metallic materials.

This project was initiated by EPA but is now funded by Task Group VII, Effects on Materials and Cultural Resources, within the National Acid Precipitation Assessment Program.

## Introduction

At a material exposure site located at the Research Triangle Park, N.C., in 1982, the Environmental Protection Agency began a study on the effects of dry and wet deposition on panels of galvanized steel and Corten A weathering steel. The objective of this study was to use an automatic covering device as a means to partition the effects of dry and wet deposition during exposure of these materials. Duplicate sets of panels were prepared for each material. One set of panels was covered by the automatic device only during each rain event. The other set of panels was boldly exposed to both dry and wet deposition at the site. Corrosion of the metals was determined from weight loss measurements. Air quality and meteorological parameters were continuously monitored and reported as hourly averages at the site. Collections of rain and particles are also analyzed and reported. Multiple regression techniques were used to determine the factors that were statistically significant. Models were developed to explain how dry and wet deposition factors affect the corrosion rates of galvanized and weathering steels.

## Experimental

### Material Selection and Preparation

Both weathering steel and galvanized steel are used for exterior applications. Weathering steel was developed for use in unpainted architectural and structural designs. The weathering steel selected for exposure in this study was Corten A, a product of U.S. Steel Corporation. Commercial grade 20 gauge galvanized steel sheet was selected for exposure.

For both metals, 10 by 15 cm panels were sheared from sheet stock. Panels of both metals were individually identified by a code stenciled lightly on the ground exposure side. Prior to field exposure, the galvanized steel panels were cleaned by immersion for approximately 2 minutes in 10% by weight of ammonium chloride solution at a temperature of 60-80°C (1). The weathering steel panels were immersed in Clark's solution until the scale was visually removed (1). Panels of both metals were rinsed in deionized water and then with methanol to remove moisture. After drying each panel was weighed to 0.1 mg.

Exposure Procedure

The weathering steel and galvanized steel panels were exposed at 30° to the horizontal (2). All panels were exposed in triplicate between ceramic insulators facing south for periods of 6, 12, 24 and 36 months. The weathering steel was also exposed for 18 and 30 months. The six-month panels were continually replaced with new panels in order to study the effects of dry and wet deposition during winter and summer months.

Duplicate sets of the weathering steel and galvanized steel panels were exposed at the RTP, N.C. site. An automatic device, which is triggered by the sensor on a rain bucket collector, was used to cover one set of panels only during each rain event. This set of panels was exposed primarily to dry deposition. The other set of panels was not covered during rain events and was exposed to both dry and wet deposition processes.

Three panels of each material were removed after each exposure period. The weathering steel and galvanized steel panels were cleaned according to the procedures used prior to exposure. However, it was necessary to immerse and weigh each panel of both metals several times to ensure removal of corro-

sion products. The weights were corrected for loss of base metal in accordance with ASTM Recommended Practice (1). Each of the panels were weighed to 0.1 mg.

Environmental Monitoring

The environmental parameters, specifically air quality, including particles, meteorology, and rain chemistry that are being monitored at the Research Triangle Park, N.C. exposure site along with the reporting format are shown in Table 1.

TABLE 1--Environmental parameters measured at RTP, N.C. exposure sites

| Parameters | Reporting format |
|---|---|
| Air Quality: | |
| Continuous $SO_2$, NO, $NO_x$, $NO_2$, $O_3$ | Hourly average |
| Particulate chemistry: mass, size, composition | Weekly analysis |
| Meteorology: | |
| Weather: wind speed (WS) and wind direction (WD), temperature (T), relative humidity (RH) precipitation, solar radiation | Hourly average |
| Rain Chemistry: | |
| pH | |
| Cations | |
| Anion | Monthly analysis |

Ambient concentrations of $SO_2$, $O_3$ and $NO_x$ ($NO_2$ and NO) are being continuously monitored at the site by instruments that are approved by EPA as designated reference or equivalent methods. A technique for intermittent sampling of particles over a 7-10 day period using a dichotomous and hi-vol sampling system was developed for characterizing particulate into coarse (2.5 to 10 μm), fine (less than 2.5 μm) and total mass size fractions. Sampling

of particulate was initiated in early 1985 at the site. The meteorological parameters are continuously monitored by a Climatronics Weather Station. An Aerochem Metrics wet and dry precipitation collector is used to collect monthly rainfall for analysis.

Through a contract with EPA, the Research Triangle Institute (RTI) operated the air quality, meteorology, and rain chemistry instrumentation and insured the quality of the environmental data. Northrop Services Inc. (NSI) operated the particle sampling device and provided the analysis. In addition to the routine calibration checks that RTI and NSI performed on the environmental systems at sites, an independent system and performance audit was conducted annually.

Analysis of Environmental Data

The environmental data base was found to contain errors and missing hourly averages of air quality and meteorological data that occurred when monitoring instrumentation was either not operational or in need of calibration. A methodology, similar to that previously reported (3), was used to make corrections to the environmental data base. Climatological data from the Raleigh-Durham (RDU) Airport (about 8 km from the site) was used in this analysis of the meteorological data.

Dew point (one of the most important environmental parameters) was measured with a lithium chloride sensor for which the manufacturer specified an accuracy of only plus or minus 3°C. Averages during exposure periods from these data were consistently lower than averages of dew points for the same periods at the Raleigh-Durham Airport. In contrast there was very little difference in comparable temperatures. Calculated relative humidities using the raw RTI data were often less than 85% during periods of rain. From such calculations the fraction of time that 85% relative humidity was exceeded was

much less than expected. Because of this systematic bias, all of the dew point data were adjusted by adding 1.1°C. This change approximately doubled the calculated times of wetness and eliminated rain-relative humidity inconsistencies. In the summer of 1985, a cooled mirror dew point sensor was added to the site.

Monthly total collections as well as hourly collections for each rain event were recorded at the site. Both sets of data were used in conjunction with the RDU Airport rainfall data to provide a corrected rainfall data base.

Pollutant Fluxes

The corrosion of galvanized and weathering steel is expected to be a function of the amounts of the pollutants reaching the metal surface and the moisture conditions of the surface. The amount of a pollutant deposited is the product of the ambient concentration and the deposition velocity. From theory, Haynie (3) estimated the deposition velocity from wind speed data measured at the site. The following empirical relationship was developed:

$$u = 0.36WS^{0.86} \quad (1)$$

where u is deposition velocity in cm/sec

WS is wind speed in m/sec

Hourly deposition velocities, which were computed from equation 1 were multiplied by hourly gaseous pollutant concentrations to obtain hourly fluxes. These values were summed over the exposure periods for hours of wetness when relative humidities exceeded 85 and 90% and when the dew point was greater than 0°C. Hourly relative humidities were calculated from the temperature and dew point data.

Atmospheric particle concentrations were not measured at this site until 1985. In February, weekly samples were begun using a dichotomous sampler and

a Hi-vol. The size fraction ranges were approximately 0 to 2.5 micrometers diameter, 2.5 to 10 micrometers and 0 to about 100 micrometers. The overall annual average concentrations for the size ranges were <2.5 micrometers - 16.9 $\mu g/m^3$, 2.5 to 10 micrometers - 10.6 $\mu g/m^3$ and total suspended particulate matter (TSP) - 37.5 $\mu g/m^3$. By difference there is just as much material above 10 micrometers in the coarse mode fraction as there is below 10 micrometers, indicating that the mass median diameter for this mode is 10 μm.

Some exposures were divided into winter and summer months. The average concentrations for the fine and coarse modes were respectively for winter, 14.5 $\mu g/m^3$ and 17.7 $\mu g/m^3$ and for summer, 18.6 $\mu g/m^3$ and 22.0 $\mu g/m^3$. The average deposition velocity for the fine mode is expected to be less than 0.02 cm/sec while the deposition velocity of the coarse mode to a horizontal surface should be based on the terminal gravitational settling velocity. Assuming a mass median diameter of 10 μm, a geometric standard deviation of 2, and a density of 2 $gm/cm^3$ an average deposition velocity of 1.66 cm/sec was calculated for the coarse mode. With these concentrations, deposition velocities, specimen angle, and exposure times, particle accumulations can be calculated. The coarse mode deposition is at least two orders of magnitude greater than the fine mode deposition.

Chemical analysis showed that nearly 20% of TSP is sulfate ions and 75% of that is in the fine mode. Only about 9% of the coarse mode is sulfate ions.

## Theoretical Considerations

During atmospheric exposure, galvanized steel and weathering steel form surface films of corrosion products. These films tend to restrict the rate of corrosion by forming a protective surface layer. The rate of corrosion would then be diffusion-controlled and depend upon the thickness of the film.

When the corrosion products of the film are insoluble and do not change during exposure, the corrosion-time function is expected to be parabolic ($C = \alpha\sqrt{t}$). However, many of the known corrosion products, particularly the carbonates, hydroxides, etc. within the film are soluble in acidic solutions. In environments where acidity such as acid rain, $SO_2$, etc. is present, dissolution of the protective surface film is a competing mechanism that accelerates the rate of corrosion. Under these exposure conditions, the corrosion-time relationship can be empirically expressed as (5,6):

$$C = At^n \tag{2}$$

where C is a measure of corrosion, t is time, and A and n are empirical coefficients. The n coefficient usually has a value between 0.5 and 1.0.

The mathematical solution to the differential equation describing the mechanism of competing formation and dissolution of the protective film is the transcendental function (4):

$$C = bt + a[1-\exp(-bc/a)]/b \tag{3}$$

which is equivalent to:

$$C = bt + a/(dc/dt) \tag{4}$$

where coefficient, b, is the rate of dissolution of the protective film which is a function of the rate of delivery of the reacting pollutants to the surface and coefficient, a, is a function of diffusivities through the film which can also be affected by pollutants.

The effects of environmental factors on the coefficients a and b cannot be determined by a least squares fit of equation 3. As a/b becomes large,

equation 3 approaches an identity. When bc/a is large, exp(-bc/a) approaches zero and equation 2 becomes:

$$C = bt + a/b \tag{5}$$

Equation 4 is linear with a/b being the intercept and b being the slope.

Galvanized Steel: When exposed in a polluted environment, galvanized steel exhibits linear corrosion behavior (7). In non-polluted environments, the corrosion-time curve may have some observable curvature during the first year of exposure. The linear corrosion behavior of galvanized steel indicates the rate of formation of the protective film is equal to the rate of dissolution. Zinc carbonate that forms in the protective film on galvanized steel can be dissolved during rain. The solubility of zinc carbonate is dependent on the concentration of $CO_2$ in the solutions (8) which is dependent on the atmospheric concentration of $CO_2$. As the temperature increases the solubility of $CO_2$ in water decreases (9).

Following a textbook example for the thermodynamics of metal carbonates (10), it can be shown that the overall reaction simplifies to:

$$ZnCO_{3(c)} + H_2O_{(1)} + CO_{2(g)} = Zn^{++} + 2HCO_3^- \tag{6}$$

The equilibrium equation assuming unit activity for both zinc carbonate and water and an ion balance is:

$$Zn^{++} = (K[CO_{2(g)}]/4)^{1/3} \tag{7}$$

where $Zn^{++}$ is gm moles/liter and $[CO_{2(g)}]$ is atmospheres of $CO_2$ in air.

From thermodynamic considerations and solubility data (8,9), the equilibrium constant K is related to temperature by the relationship:

$$K = \exp(-76.476 + 7035/T + 6.354\ \ln T) \tag{8}$$

where T is absolute temperature - °K

The corrosion of zinc is reported to be stoichiometrically proportional to the amount of $SO_2$ deposited during periods of wetness (i.e. dew) (11,12).

A theoretical coefficient of .00143 is calculated when $SO_2$ is expressed as $\mu g/cm^2$ and corrosion in $\mu$.

Weathering Steel: Most of the corrosion products of weathering steel is retained in the film during the first few years of exposure. During the early corrosion stages of weathering steel, equation 3 becomes:

$$C = bt + at/nc \qquad (9)$$

where $dc/dt \simeq nc/t$ (empirical relationship)

If a/nc is greater than b, most of the corrosion products remain in the film and the corrosion-time function should be parabolic. Except when the protective film stays wet, the film becomes more protective with time. During extended periods of wetness, the corrosion of weathering steel is not much better than carbon steels.

## Results

The corrosion results for different corrosion periods are presented in Table 2. The covered weathering steel corroded more than the uncovered steel. Over the range of exposures, corrosion is generally linear with time. During the initial six months of exposure, however, the corrosion rates of both metals are considerably greater than they are afterwards.

The environmental data for the 36-month exposure period are given in Table 3. Similar averages were calculated for all exposure periods.

TABLE 2--Corrosion of covered and uncovered weathering steel and galvanized steel at the Research Triangle Institute site

| | Start Date | End Date | Total Time | Time >85% | Time >90% | Rain | Weathering Steel | Galvanized Steel |
|---|---|---|---|---|---|---|---|---|
| | | | hrs. | hrs. | hrs. | cm | μm | μm |
| Covered | 82/10/19 | 83/05/04 | 4752 | 1468 | 1220 | | 13.739 | 0.231 |
| | 83/05/05 | 83/11/03 | 4392 | 1427 | 977 | | 12.244 | 0.276 |
| | 83/11/04 | 84/05/01 | 4320 | 850 | 675 | | 12.642 | 0.329 |
| | 84/05/02 | 84/11/05 | 4512 | 1695 | 992 | | 12.861 | 0.253 |
| | 82/10/19 | 83/11/03 | 9144 | 2894 | 2197 | | 21.364 | 0.320 |
| | 84/11/06 | 85/10/09 | 8122 | 1579 | 1025 | | | 0.261 |
| | 84/11/06 | 85/10/31 | 8640 | 1642 | 1040 | | 22.830 | |
| | 83/05/05 | 84/11/05 | 13224 | 3971 | 2644 | | 21.165 | |
| | 82/10/19 | 84/11/05 | 17976 | 5439 | 3864 | | 30.250 | 0.614 |
| | 83/05/05 | 85/10/31 | 21846 | 5613 | 3684 | | 29.811 | |
| | 82/10/19 | 85/10/09 | 26088 | 7018 | 4889 | | | 0.668 |
| | 82/10/19 | 85/10/31 | 26616 | 7081 | 4904 | | 35.528 | |
| Uncovered | 82/10/19 | 83/05/04 | 4752 | 1491 | 1257 | 65.91 | 11.793 | 0.365 |
| | 83/10/19 | 83/11/03 | 4392 | 1462 | 1031 | 44.71 | 11.766 | 0.302 |
| | 83/11/04 | 84/05/01 | 4320 | 906 | 751 | 80.70 | 11.054 | 0.462 |
| | 84/05/02 | 84/11/05 | 4512 | 1719 | 1051 | 50.21 | 11.925 | 0.396 |
| | 82/10/19 | 83/11/03 | 9144 | 2953 | 2288 | 110.63 | 20.061 | 0.645 |
| | 82/10/19 | 83/10/09 | 8112 | 1731 | 1224 | 82.82 | | 0.494 |
| | 84/11/06 | 85/10/31 | 8640 | 1800 | 1245 | 83.86 | 18.267 | |
| | 83/05/05 | 84/11/05 | 13224 | 4087 | 2833 | 175.62 | 17.681 | |
| | 82/10/19 | 84/11/05 | 17976 | 5578 | 4090 | 241.53 | 25.116 | 1.227 |
| | 83/05/05 | 85/10/31 | 21846 | 5587 | 4078 | 259.48 | 22.827 | |
| | 82/10/19 | 85/10/09 | 26088 | 7309 | 5314 | 324.14 | | 1.442 |
| | 82/10/19 | 85/10/31 | 26616 | 7378 | 5335 | 325.90 | 28.890 | |

TABLE 3--Average environmental conditions for 36-month exposure period

| Factor | Averages | | | | | | |
|---|---|---|---|---|---|---|---|
| | Total Time | When Wet* | | | | | |
| | | RH>80 | | RH>85 | | RH>90 | |
| | | with rain | without rain | with rain | without rain | with rain | without rain |
| Temperature °C | 15.1 | 15.1 | 15.0 | 14.6 | 14.6 | 13.9 | 13.7 |
| Dew Point °C | 8.7 | 13.5 | 13.5 | 13.4 | 13.5 | 13.0 | 13.0 |
| Relative Humidity % | 69.1 | 90.5 | 90.8 | 92.4 | 93.1 | 94.3 | 95.6 |
| Windspeed - m/sec | 1.59 | 1.17 | 1.15 | 1.17 | 1.14 | 1.19 | 1.12 |
| Deposition Velocity cm/sec | 0.514 | 0.392 | 0.387 | 0.391 | 0.382 | 0.397 | 0.377 |
| $SO_2$ $\mu g/m^3$ | 8.02 | 5.00 | 5.00 | 4.77 | 4.77 | 4.47 | 4.43 |
| $NO_x$ as $NO_2$ $\mu g/m^3$ | 42.7 | 46.4 | 46.6 | 46.4 | 47.2 | 47.6 | 48.9 |
| $SO_2$ flux $\mu g/cm^2 y$ | 0.1437 | 0.0660 | 0.0651 | 0.0635 | 0.0617 | 0.0619 | 0.0582 |
| $NO_x$ flux $\mu g/cm^2 y$ | 0.4343 | 0.3686 | 0.3673 | 0.3706 | 0.3663 | 0.3804 | 0.3739 |
| Fraction when wet | | 0.347 | 0.340 | 0.277 | 0.266 | 0.200 | 0.184 |

*Dew point is greater than 0°C.

It should be noted that values for both $SO_2$ concentration and deposition velocity are significantly lower during periods of wetness than are the averages for total time of exposure. The deposition velocities and fluxes are the calculated turbulent movement toward the specimen surface and not net diffusion. When surfaces are dry, $SO_2$ will absorb until a monolayer is built up (12). After that the net flux will be zero (movement away equals movement toward). During wetness periods, $SO_2$ is either consumed to form a sulfate or catalyzed to non-volatile sulfuric acid so that the net flux approaches the turbulent flux toward the surface. The drop in $SO_2$ concentration during periods of wetness is evidence that the rate of removal from the atmosphere is much faster than it is when dry. In contrast, $NO_x$ concentrations do not change significantly because the net flux is extremely low, even during periods of wetness (13).

The average rain chemistry and loadings on specimens for the 36-month period are given in Table 4.

TABLE 4--Average rain chemistry and loadings on weathering steel and galvanized steel corrosion specimens for 36-month exposure

| Ion | Concentration μ-moles/liter | Specimen Loading* μ-moles/cm$^2$ |
|---|---|---|
| $H^+$ | 38.20 | 5.38 |
| $Ca^{++}$ | 2.37 | 0.33 |
| $Mg^{++}$ | 1.39 | 0.20 |
| $K^+$ | 0.77 | 0.11 |
| $Na^+$ | 9.25 | 1.30 |
| $NH_4^+$ | 10.47 | 1.47 |
| $NO_3^-$ | 16.35 | 2.30 |
| $Cl^=$ | 11.66 | 1.64 |
| $SO_4$ | 18.55 | 2.61 |
| $PO_4$ | 0.10 | 0.01 |
| pH | 4.42 | |

*Rain is assumed to fall vertically on the skyward side of the specimens mounted at a 30° angle to the horizontal. Thus, the average loading for both sides is 0.5 cos 30 times the loading on a skyward horizontal surface.

Similar averages were calculated for all exposure periods. The range of concentrations varied by less than a factor of 2.5. The average pH ranged from 4.19 to 4.58.

## Analysis of Results

A chemical species can deposit on a surface as a gas during periods of wetness and dryness, in rain, and in particulate matter. The relative potentials for corrosion can be compared by calculating loadings for each mechanism of delivery. The potential corrosion of zinc is used as an example.

Sulfur dioxide gas and sulfates are assumed to react stoichiometrically with zinc. The dissolution of zinc carbonate in rain is assumed to follow equations 6 and 7 with the concentration of $CO_2$ in the atmosphere being 300 ppm. Only coarse mode particles deposit on the skyward surface. Sulfur dioxide deposition during dryness is limited to a monolayer on the surface which includes the increased surface area of accumulated particles. Rain

tends to wash off the particles from the boldly exposed specimens, but over three years of exposure the total surface area of the covered specimens can be nearly doubled. Sulfur dioxide deposition is turbulent diffusion controlled when the dew point is greater than zero and the relative humidity is greater than 90% or it is raining. Hydrogen ions are consumed in the depolarization of the cathodic half cell reaction for the corrosion of zinc. Based on these assumptions, the relative potentials for zinc corrosion for the three year period at RTI are presented in Table 5.

TABLE 5--Potential contributions to zinc corrosion at RTI site for three year period

| Mechanism | | Zinc Corrosion - μm covered | uncovered | |
|---|---|---|---|---|
| Dry Deposition | Particle sulfate | 0.1151 | 0.1151 | |
| | $SO_2$ when dry | 0.2427 | 0.1243 | |
| | $SO_2$ when wet | 0.0463 | 0.0538 | |
| | Subtotal | 0.4041 | 0.2932 | |
| Rain | $ZnCO_3$ solubility | | 0.6855 | |
| | Rain sulfate (anodic reaction) | | 0.2390 | 0.2427 avg. |
| | $H^+$ (cathodic reaction) | | 0.2463 | |
| | Subtotal | | 0.9282 | Diff. |
| | Total | 0.4041 | 1.2214 | 0.8173 |
| Actual Corrosion | | 0.668 | 1.442 | 0.774 |

The calculated difference between the covered and uncovered specimens is very close to the actual difference. The actual corrosion values should be greater than the calculated values because they include the removal of insoluble corrosion product film during the specimen cleaning process and the possibility of $ZnCO_3$ solubility and runoff in dew. From weights taken prior to cleaning, assuming the film was zinc carbonate, an equivalent zinc loss for the covered and uncovered specimens was 0.278 μ and 0.272 μ respectively. When these amounts are added to the calculated values, there is good agreement with the actual values.

At this relatively unpolluted site (except for rain acidity), 76% of zinc corrosion of these specimens is potentially caused by rain. Seventy-four percent of that corrosion could be caused by clean rain.

Similar calculations cannot be made for weathering steel because pollutant effects are not stoichiometric. Rust catalyzes the conversion of $SO_2$ into sulfuric acid in the presence of moisture. Iron sulfates are not stable in the presence of oxygen and moisture.

Statistical Analysis

The high degree of covariance between possibly contributing environmental factors, limited ranges of variables and limited number of data sets makes it unlikely that significant coefficients can be obtained from multiple regression analysis when all the variables are included. With only eight sets of data, either covered or uncovered, for galvanized steel, and ten sets for weathering steel, no more than three variables are expected to have significant coefficients. This does not mean that factors without statistically significant coefficients do not actually contribute to corrosion.

Weathering steel: Several multiple regression models were analyzed for corrosion of weathering steel. The only variable other than time that was

consistently statistically significant was rain. The best fit of the data with statistical significance was obtained with a model:

$$\ln(\text{Steel}) = a_0 + a_1\text{Rain/Time} + a_2\ln(\text{Time}) \quad (10)$$

where steel is weathering steel corrosion in micrometers, Rain is amount of rain in centimeters and Time is exposure time in years. The results of the regression analysis are in Table 6.

TABLE 6--Regression analysis of the equation:

$$\ln(\text{Steel}) = a_0 + a_1\text{Rain/Time} + a_2\ln(\text{Time})^*$$

| Variable | | Coefficient | Standard error | t-statistic |
|---|---|---|---|---|
| | ($a_0$) | 2.957 | | |
| Rain/Time | ($a_1$) | -0.001373 | $\pm$0.000378 | -3.63 |
| ln(Time | ($a_2$) | 0.516 | $\pm$0.032 | 16.01 |

*$R^2$ = 0.9414

Exposure time alone does not corrode steel. Factors such as pollutant accumulations and time-of-wetness are highly covariant with time and could contribute to corrosion. The relative magnitude of error in these factors with respect to time possibly excluded them from a best fit regression. Rain reduces the corrosion of weathering steel, possibly by washing away the accumulation of acidic species.

Galvanized Steel: The model for galvanized steel corrosion is that which was used to produce Table 5. The factors; 1) particle sulfate accumulation, 2) $SO_2$ accumulation when dry, 3) $SO_2$ accumulation in dew, 4) $ZnCO_3$ dissolution by $CO_2$ in rain, and 5) the average of sulfate and hydrogen ion in rain were coverted to stoichiometric equivalent zinc corrosion thickness losses. The first three were added to create the dry deposition factor and

the last two to create the rain factor. Both of these factors were added to produce a total expected effect.

When a stepwise multiple linear regression of galvanized steel was done considering these factors individually and in combination, the total expected effect was selected as most statistically significant. The slope coefficient was 1.0131 $\pm$ 0.0517 which is very close to the theoretically expected value of one. The intercept was 0.1988 which represents the zinc in an average steady state thickness of the corrosion product film. The $R^2$ for the regression is 0.965.

Multiple regressions were done on several combinations of factors that make up the total expected effect. Because of the high degree of covariance between factors, a factor might have a coefficient greater than one while another for which it is acting as a proxy would have a value less than one and not be statistically significant. The rain factor was consistently statistically significant and close to a value of one in all of these regressions.

## Discussion of Results

In this three-year exposure study, an automatic covering device was examined as a possible means for partitioning the effects of wet and dry deposition on the corrosion of galvanized steel and weathering steel. When galvanized steel and weathering steel are exposed, a protective surface film forms that retards further corrosion of the metal. Many of the corrosion products within the protective film are soluble in acidic solution. In environments where increased acidity is present, dissolution of the protective film is a competing reaction that can accelerate the rate of corrosion of these metals. The materials exposure site at the Research Triangle Park, NC

site, is a clean rural site, especially in regards to atmospheric loadiangs of $SO_2$. The average pH of annual rainfall at the site is about 4.4 which is typical of the eastern United States.

Because of the short exposure period and the covariance between contributing environmental factors, statistical analysis, particular multiple regression techniques, was limited. For the corrosion of weathering steel, an exponential function was derived where rainfall and time of exposure were found to explain better than 94% of the variability. The coefficient for rainfall was negative which is consistent with prior studies of weathering steel (4). It is apparent that rainfall is removing corrosive agents, especially acids, thereby retarding the rate of corrosion of weathering steel that was observed for the uncovered exposure during this study.

For the corrosion of galvanized steel, particle sulfate accumulation, $SO_2$ accumulation when dry, and $SO_2$ accumulation in dew are important factors for the dry deposition component. Whereas, sulfate and hydrogen ions in rain and $ZnCO_3$ dissolution by $CO_2$ in rain are factors for the wet deposition. The coefficient for the slope of a linear model using the wet and dry deposition factors was consistent with theory. Wet deposition can potentially cause 76% of the corrosion of galvanized steel at this site.

## Conclusions

The covering device appears to provide a means to partition the effects of dry and wet deposition during the field exposure of galvanized steel and weathering steel. Wet deposition is having an effect on the corrosion of those metallic materials at the Research Triangle Park site. An additional exposure condition of spraying test samples with pH 5.6 simulated clean

rain during the rain event will be needed to enable the effects of rain acidity on the corrosion of metallic materials to be quantified.

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